Title: Science-Based Methods to Assess Risks Attributable to Petroleum Residues Transferred from Soil to Vegetation

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Statement of Problem: Risk-based decision making is increasingly used in the United States and around the world for managing hydrocarbon impacted soils at exploration and production sites. Risk assessments of contaminated soils often rely on models that link soil residue levels to exposure concentrations in vegetation. Currently, these models use empirical relationships developed from a relatively small number of plant species and chemicals (mostly chlorinated hydrocarbons). Uptake into vegetation is often assumed to follow a simple plant-soil partitioning relationship derived from the octanol/water partition coefficient, which is used as a surrogate for a chemical's relative lipid-water solubility. Existing models ignore mass transfer and transformation processes and variations among vegetation types. As a result, linking chemical residues in soil to exposure concentrations for food or feed has a level of uncertainty that is extremely high. Very little quantitative information is available for reducing this uncertainty. Without an improved understanding of the mechanisms of plant uptake, the credibility of current risk-based analyses of soil residues will remain limited and models of ecological and human risk will remain highly conservative—often leading to exceedingly low risk-based screening levels in soil. The objectives of this project are to develop and apply a reliable experimental approach for studying plant uptake to produce relevant experimental data that will reduce uncertainty in exposure and risk models for petroleum contaminated soils.

Comparison of New Technology to Existing Technologies: Although a number of published reviews relating to various aspects of plant uptake are available, existing technologies (i.e. models and databases) for estimating biotransfer have not been evaluated for their applicability to hydrocarbon impacted soils. When measured biotransfer factors (BTFs) are lacking, which is most often the case, empirically-based plant-soil partition coefficients are used to link soil residues to exposure concentrations in food or feed. The same empirical relationship is used in all existing regulatory environmental models (i.e., TRIM.FaTE, 3MRA, IEM-2M, Eco-SSL). The existing plant uptake models ignore transformation processes, possible sequestration in plant tissue and variations among vegetation types. The new modeling technology and data that will be developed in this work will provide a systematic and comprehensive evaluation of both direct (soil↔plant) and indirect (soil↔air↔plant) transfers of soil-borne contaminants into vegetation. The work will use existing data and theory as well as new data from controlled exposure experiments. The new information will support development of a more process-based model of plant uptake that will improve our understanding of the relative contribution of chemical uptake (gains) and transformation or sequestration (losses) to observed bioaccumulation in above-ground vegetation.

Application and Benefits to Industry: Recent work in the Petroleum Environmental Research Forum (PERF) (e.g. PERF 94-06, 97-08 and 99-13) has focused on improving the use of science and risk-based decision making at oil and natural gas exploration and productions sites internationally. This proposal supports the efforts of PERF 99-13 by improving the science that supports risk-based decision making. Uncertainties about the link between chemical residues in soil and human or ecological exposure can lead to overly conservative risk-based screening levels that degrade the credibility of the overall risk-based approach. This project is aimed at reducing these uncertainties with the primary focus on improving the reliability of risk assessments for contaminated soil where the critical and (often) most uncertain exposure pathway is the accumulation of chemicals in plants. Reducing this uncertainty will reduce the need for conservatism without degrading confidence that public health and the environment are protected.

Of particular value to industry is our use of a highly controlled experimental system that provides a unique opportunity to examine the combined role of uptake through multiple pathways and loss through transformation over the full lifecycle of the plant. Previous experimental and modeling systems have focused on chemical uptake with little effort to quantify important transformation processes such as metabolism within plants and the sequestering of chemicals into non-available forms. Our efforts to explicitly measure both uptake and loss will provide an important opportunity to revisit and revise regulatory models that ignore these pathways. The data generated through this research is expected increase the reliability of predictive models for evaluating food-chain exposure pathways. The main benefits to industry will be increased confidence in models that link soil residues to exposure and risk. The results will support the move towards an increased use of risk and risk-benefit concepts by industry, government, and public health organizations.

Tasks and Contributions of the Research Team: Research has shown that residues in soil can be transferred to food chains through vegetation. However, many chemicals of concern are transformed or sequestered in vegetation in ways that lower potential risk. The role of vegetation in controlling fate, exposure and dose remains highly uncertain but limited experiments reveal that measured biotransfer ratios between soil and plants are often lower than default predictions from existing empirical models. Existing models do not account for degradation and/or sequestration in plants. The primary contribution

from this project will be new data from experiments designed specifically to confront many of these limitations with particular emphasis on petroleum hydrocarbons impacted soils.

Task 1: The first task of this proposal is a comprehensive and ongoing review of the scientific literature to evaluate existing models, theory and screening approaches for plant uptake and how they apply to soils impacted by petroleum hydrocarbons. This review will include an analysis of existing data (both from the published literature and reports identified by our industry and academic partners) to better characterize the strengths and limitations of current modeling approaches. The analysis and review will culminate in a revised plant uptake model that will be used to identify critical data gaps in the plant uptake literature. The revised model will be semi-mechanistic and will help guide the design of the experimental phase of this work. The revised model will also provide an initial tool for interpretation of experiments.

Task 2: Competing pathways, a large number of environmental variables and the overall complexity of the soil/plant/air system make it difficult to use field studies, or short-term lab studies, to understand the factors controlling pollutant uptake in plants. The second task of this project will develop controlled experimental exposure chambers to better characterize the mechanistic basis of plant uptake. This task will build upon two existing exposure chambers designed and used in collaborations between LBNL and the University of California. The chambers allow control and monitoring of chemical concentrations in the source medium and the exposed vegetation over extended growth periods and provide a means to minimize the transfer of ambient pollutants into the exposure system. These chambers provide a unique opportunity to examine the combined role of uptake and transformation in plants under relevant exposure conditions and duration.

Task 3: The results from the chamber studies will be used along with the extensive modeling capabilities at LBNL to evaluate the mechanistic basis of plant uptake and develop/recommend a method or model for evaluating the transfer of soil residues into food chains. The results will be communicated through peer-reviewed journals, conference presentations and workshop participation with our industry partners. In the final year of the project (FY04) the measured bioconcentration ratios for the set of test chemicals will be reported. The experimental data combined with the ongoing literature review are expected to result in a more reliable and mechanistically based modeling system for plant uptake.

Deliverables: (1) During FY02, our findings on the state of the science for predicting bioaccumulation of soil residues in plants were presented at scientific conferences, through participation in an industry workshop and in the form of a draft manuscript that is in preparation. (2) During FY03 we finished development of the process-based plant uptake model, setup the exposure chamber system, developed the chemical extraction and analysis methods, began the experimental phase of the project, completed the exposure and sample collection phase of a plant uptake study, and initiated sample workup. We also continued work on the review paper and presented initial findings at a scientific conference. (3) During FY04, we will complete the sample analysis; interpret the results using statistical and process models, and then draft a manuscript reporting plant/soil concentration ratios for a set of polycyclic aromatic hydrocarbons and n-alkanes. The manuscript will present a revised modeling approach for predicting the bioaccumulation potential of petroleum hydrocarbons in plants. Results from the chamber experiments in combination with field data from our industry and academic partners will provide a valuable repository of data for developing and experimentally validating models for estimating the extent of accumulation of petroleum hydrocarbons in human and ecological food webs. The approach will also provide a framework for future studies that extend this work to other plants, soil types, chemicals and environmental conditions.

Why DOE Should Support Project: Within the oil industry there are active research programs that have generated experimental data on the uptake of petroleum hydrocarbons into biota. However, industry lacks the scientific links to the regulatory agencies and the academic institutions needed to communicate information to key regulatory personnel. Although such expertise resides at LBNL, industry does not have the mechanism or resources to support the type of basic experimental and modeling research needed to understand the plant uptake issue. LBNL is uniquely positioned to provide cutting edge research that combines controlled experimental exposure studies with environmental and statistical modeling to improve risk-based decision making at contaminated industrial sites and sites within the DOE complex. Support from DOE to LBNL provides the best mechanism to foster synergy between National Lab expertise and ongoing Industry research on the uptake of soil-borne contaminants into food chains. Lab support of the partnership will optimize the use of scarce resources in a way that provides regulatory flexibility while assuring protection of public health and the environment.

Critical Decision Points: The first decision point came at the end of FY02, following the completion of our preliminary review of existing models and data. We have evaluated the limitations of these models when applied at petroleum contaminated sites and found that that existing methods are highly uncertain and may over-predict the plant uptake of many of the chemicals that are most relevant for petroleum impacted soils. It was determined that controlled experimental studies were needed to evaluate the mechanistic basis of plant uptake. LBNL in consultation with researchers at ChevronTexaco decided to focus the initial experimental phase of the study on the grass/soil relationship because of the importance of grass in both agricultural and ecological systems. The partnership also decided to incorporate n-alkanes into the study design to evaluate the impact of co-pollutants on uptake of PAHs. After updating the model based on results from the experiments, the need to continue the chamber studies using different plants, chemicals and soils will be evaluated. This decision to continue will be based on the level of uncertainty remaining in the models and statistical analysis used to identify the types and amount of additional information that would provide the greatest improvement in the accuracy and precision of plant uptake models.

Accomplishments, Milestones and Deliverables from FY02&FY03 and proposed for FY04:

Proposed accomplishments for FY02 included a review of the literature on plant uptake models with particular emphasis on petroleum hydrocarbon impacted soils; compilation of existing data on plant uptake for polycyclic aromatic hydrocarbons; development of a prototype semi-process based plant uptake model; and begin setup/calibration of exposure chambers for use in experimental phase of the project. All of the proposed accomplishments for FY02 have been completed. A paper introducing the use of the controlled environmental exposure chambers for isolating and evaluating the different plant uptake pathways was published (Maddalena et. al., 2002). Initial findings from the literature review and data evaluation were presented to industry (Maddalena and McKone, 2002) and the development and evaluation of a semi-process based plant uptake model was presented (Maddalena and Sohn, 2002). Preparation of the review manuscript is ongoing.

Proposed accomplishments for FY03 included finishing development of the controlled chamber system for evaluating the multi-pathway uptake of soil-borne hydrocarbons into vegetation; preparation of spiked agricultural soils; development of methods for extraction and analysis of test chemicals in samples collected during exposure studies; completion of the exposure phase of initial plant uptake experiment; and initial evaluation of measurements.

Two changes were made to the original proposed accomplishments for FY03. First, LBNL researchers, in consultation with researchers at ChevronTexaco and UC Davis, elected to substitute wheat grass for the wheat grains that were initially selected as the target vegetation in the exposure studies. The substitution was made because the turnaround time for experiments using grass is much shorter than comparable experiments using wheat grains. In addition, the likelihood of successfully growing a mature crop is much higher with grass than with grain. The substitution was deemed necessary to insure that usable results could be obtained despite the reduction in funding levels in FY03 relative to the original proposal. A second change that was made to the original experimental design was the inclusion of a set of n-alkanes in the test soils. The petrogenic (i.e., even carbon number) hydrocarbons were included to evaluate the impact of co-pollutants on the resulting plant/soil concentration ratios. The chemicals were selected by LBNL researchers in consultation with industry partners at ChevronTexaco. The inclusion of n-alkanes in the study design required some modifications to the extraction/analysis methods that were under development to reduce the levels of background contaminant in the samples due to plastic containers and cartridges.

The proposed accomplishments for FY03 have been completed. A description of the extraction and analysis methods used to quantify the PAHs in air, soil and vegetation have been presented (Kabaishi et al, 2003a & b). The controlled exposure chambers are now operational and the exposure phase of the first plant uptake experiment has been completed. Initial results from the study were reported at a national scientific conference (Maddalena et al, 2003a; Kabashi et al, 2003a&b) and to industry (Maddalena et al, 2003b).

Current progress in FY04 is on schedule. Expected deliverables include completion of the review paper on uptake of petroleum hydrocarbons from soil into vegetation; complete analysis and interpretation of results from grass uptake study; and manuscript reporting the measured plant/soil concentration ratios along with results from the process-based uptake model.

Current list of Accomplishments

All accomplishments are reported in the following journal papers and presentations at scientific meetings:

Maddalena, R. L.; T. E. McKone and N. Y. Kado, "Exposure Chamber Measurements of Mass Transfer and Partitioning at the Plant/Air Interface" *Environmental Science and Technology* 2002, 36, 3577-3585.

Maddalena, R. L. and M.D. Sohn,"Extending Sensitivity Analysis Methods beyond the Input/Output Relationship" ISEA/ISEE Conference. Vancouver BC 2002.

Maddalena, R. L. and T.E. McKone, " Science-Based Methods to Assess Risks Attributable to Petroleum Residues Transferred from Soil to Vegetation" Paper presented at PERF 99-13 Annual meeting, Annandale, NJ. 2002.

Kobayashi, R.; R.A. Okamoto; R.L. Maddalena and N.Y Kado. "Measurement and Mechanism of PAH Uptake in Wheat Grains". Poster presentation at Toxic Substances Teaching and Research Program Annual Meeting, Oakland CA. 2003a.

Maddalena, R.L.; R. Kobayashi, T.E. McKone, and N.Y. Kado. "Controlled Chamber Measurements of the Multipathway Uptake of PAHs from Soil into Wheat". Paper presented at Society of Environmental Toxicology and Chemistry Annual Meeting, Austin TX. 2003a

Kobayashi, R.; R.A. Okamoto; R.L. Maddalena and N.Y Kado. "Measurement of Polycyclic Aromatic Hydrocarbons in Wheat Grains". Poster presented at Society of Environmental Toxicology and Chemistry Annual Meeting, Austin TX. 2003b.

Maddalena, R.L.; R. Kobayashi, T.E. McKone, and N.Y. Kado. "Controlled Chamber Measurements of the Multipathway Uptake of PAHs and n-alkanes from Soil into Wheat". Presentation at PERF 99-13 Annual Meeting, Richmond CA. 2003b